

TRANSITION STRENGTHS IN THE VISIBLE ABSORPTION SPECTRUM OF I₂: ONE MORE PASS

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The absorption spectrum of I₂ is examined anew across the wavelength range 400-850 nm, where there is significant room-temperature absorption in the three overlapped electronic transitions. To better characterize the discrete absorption in the dominant $B - X$ system, spectra are recorded in the 520-640-nm region with high quantitative precision (0.0005 absorbance units) at moderate resolution (0.1 nm) and are analyzed by least-squares spectral simulation, yielding the $B - X$ electronic transition strength μ_e^2 with unprecedented precision (< 2 percent relative standard error) over most of the studied region. This treatment also yields directly new estimates of the continuous absorption, which support previous assessments of the $A - X$ transition but indicate that the $C - X$ transition is 20 percent weaker than thought. In companion studies, lower resolution (1 nm) spectra and multiple-temperature absorption data from the literature are analyzed as bound-free by quantum spectral simulation, to yield estimates of the small- R potential curve extensions for all three excited states and their R -dependent transition moment functions. To increase the precision and range of description of the least-known C -state potential, the least-squares analysis is expanded to include quantum simulation of literature data for the $B - C$ predissociation. The result is a C -state potential obtained with a precision comparable to that achieved in many discrete spectroscopic studies, over the range where absorption and predissociation occur (2.5-2.9 Å), and extending smoothly to its van der Waals well at 4.3 Å.

The discrete simulation method described here is applicable to any system where the spectrum can be reliably simulated, which must include treatment of the absorption and instrumental lineshapes. The I₂ $B - X$ results are directly applicable to the monitoring of I₂ in the atmosphere.